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DISTRIBUTION OF RUBIDIUM, STRONTIUM, AND ZIRCONIUM IN TUFF FROM TWO DEEP COREHOLES AT YUCCA MOUNTAIN, NEVADA

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ABSTRACT

Variations in concentrations of trace elements Rb, Sr, and Zr within the sequence of high-silica tuff and dacitic lava beneath Yucca Mountain reflect both primary composition and secondary alteration. Rb and K concentrations have parallel trends. Rb concentrations are significantly lower within intervals containing zeolitic nonwelded to partially welded and bedded tuffs and are higher in thick moderately to densely welded zones. Sr concentrations increase with depth from about 30 ppm in the Topopah Spring Member of the Paintbrush Tuff to almost 300 ppm in the older tuffs. Zr concentrations are about 100 ppm in the Topopah Spring Member and also increase with depth to about 150 ppm in the Lithic Ridge Tuff and upper part of the older tuffs. Conspicuous local high concentrations of Sr in the lower part of the Tram Member, in the dacite lava, and in unit c of the older tuffs in USW G-1, and in the densely welded zone of the Bullfrog Member in USW GU-3/G-3 closely correlate with high concentrations of less-mobile Zr and may reflect either primary composition or elemental redistribution resulting largely from smectitic alteration. Initial $^{87}Sr/^{86}Sr$ values from composite samples increase upward in units above the Bullfrog Member of the Crater Flat Tuff. The progressive tenfold increase in Sr with depth coupled with the similarity of initial $^{87}Sr/^{86}Sr$ values within the Bullfrog Member and older units to those of Paleozoic marine carbonates are consistent with a massive influx of Sr from water derived from a Paleozoic carbonate aquifer.

INTRODUCTION

The volcanic section at Yucca Mountain is a wedge-shaped layered sequence of 15- to 11-m.y.-old tuffs and lavas; the thickest part of the sequence, inferred to exceed 3.5 km, approximately underlies the northern half of the candidate area selected for characterization as a potential site for storage of high-level nuclear waste (fig. 1).[1,2] Paleozoic carbonate rocks are known to underlie the Miocene volcanic sequence at depths as shallow as 1.2 km less than 3 km to the southeast of the candidate area and may extend beneath it.[2,3]

Coreholes USW G-1 and USW GU-3/G-3, herein referred to as "G-1" and "G-3", are outside but near the northern and southern boundaries, respectively, of the candidate area (fig. 1). The volcanic sequence was continuously cored in G-1 and G-3 to depths of 1806 m and 1533 m, respectively. Major ash-flow sheets and lavas identified in these coreholes include, in descending order, the upper Paintbrush members (undivided), and the Topopah Spring Member of the Paintbrush Tuff; rhyolite of Calico Hills; the Prow Pass, Bullfrog, and Tram Members of the Crater Flat Tuff; dacite lava; the Lithic Ridge Tuff; and the older tuffs–unit a, unit b, and unit c. These major ash-flow sheets and lavas, commonly ranging in thickness between 100 and almost 400 m, are separated by 1- to 20-m-thick intervals of bedded tuff, dominantly composed of ash-fall pyroclastic deposits.[4,5] The approximate depth to the present-day water table is 575 m in G-1 and 750 m in G-3.[6]

We intend to determine first-order variability of Rb, Sr, and Zr concentrations and of Sr isotopic compositions within bulk-rock samples from G-1 and G-3. This trace-element framework will serve as a baseline for future studies of past rock-water interaction and for assessments of the potential effectiveness of the rock mass as a natural barrier to the migration of radionuclides.

ANALYTICAL METHODS

Minor- and trace-element data were derived exclusively from the analyses of bulk-rock samples of tuffs and lavas. Gamma-ray spectrometric methods were used to interpret total K content by measuring the amount of directly proportional ^{40}K in 68 samples from G-1 and 75 samples from G-3.[7,8,9] About 600 grams of sample (-20 mesh) was used in each analysis. Accuracy and precision of results are about 2 percent plus 0.05 percent.[10]

Concentrations of Rb, Sr, and Zr were obtained from 49 samples from G-1 and 45 samples from G-3. From a 100-gram sample (-200 mesh), a split of 3 grams was analyzed by energy-dispersive x-ray fluoresence (EDXRF) using a Kevex model 5100, which utilizes a ^{109}Cd radioisotopic source. Element peaks were normalized to Compton back scatter to reduce the

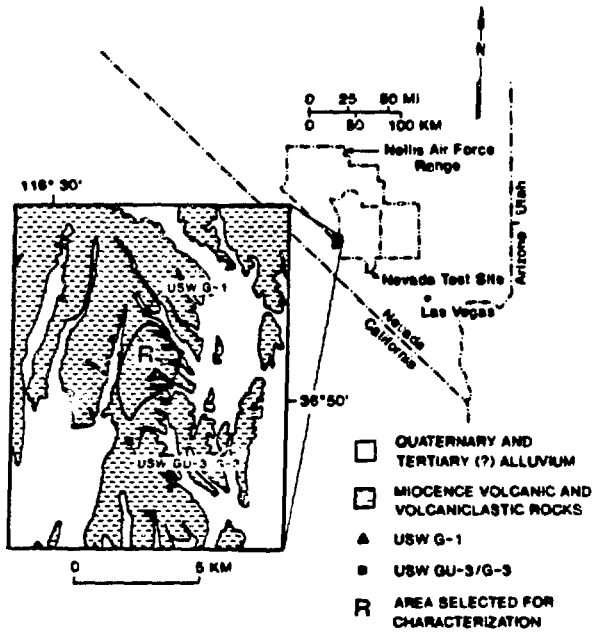

Figure 1. Map of Yucca Mountain showing the approximate location of coreholes USW G-1 and USW GU-3/G-3.

effects of matrix, particle size, and packing. Analyses of Rb, Sr, and Zr have a precision of about ±10 percent for most reported concentrations. Element concentrations of USGS rock standard GSP-1 were determined and compared after every 10-20 analyses for calibration purposes.

Composites for Sr-isotopic analysis were obtained by combining as many as 16 individual samples from each major ash-flow sheet and lava in G-1. Minor- and trace-element concentrations of composite samples were determined by EDXRF (Kevex model 770) using multiple secondary targets and USGS rock standards.[11] Mass spectrometer uncertainties in $^{87}Sr/^{86}Sr$ measurements are typically less than ± 0.01 percent.[12]

TRENDS AND CORRELATIONS

Zeolites, clays, silicates, oxides, and carbonates found in pumice, matrix, and along fractures within the tuffs and lavas are a result of the interaction of volcanic glass with infiltrating surface water, ground water, and (or) hydrothermal water.[13] Much of the alteration may have occurred concurrently with the most active period of silicic volcanism, but before to full development of the Basin-and-Range-style physiography, between 14 and 11 m.y. ago.[13] Previous mineralogic studies of the volcanic sequence have delineated four depth-dependent zones of diagenetic alteration characterized by the presence and relative abundance of specific suites of zeolites and other authigenic minerals.[14] In descending order, the four major zones of diagenetic alteration are (1) zone I, where most of the rock has remained unaltered with only minor smectite and zeolites present, (2) zone II, where much of the volcanic glass has been replaced by clinoptilolite and mordenite, (3) zone III, characterized by noticeably greater analcime, smectite, and alkali-feldspar concentrations, and (4) zone IV, where authigenic albite, alkali-feldspar, calcite, and smectite are present in significant amounts (fig. 2).[14] Distribution of altered zones and of major, minor, and trace elements are potentially influenced by (1) original chemical composition of the rock, (2) past vertical and lateral geothermal gradients, (3) past proximity to ground water, and (4) relative susceptibility of interlayered nonwelded to densely welded zones to weathering and diagenesis.[13]

Zone II, which includes most of the middle part of the volcanic section from the base of the Topopah Spring Member in G-1 and near the middle of the Prow Pass Member in G-3 downward to the base of the Tram Member in both coreholes (fig 2, 3), contains the greatest concentration of zeolites, commonly ranging between 40 and 80 percent clinoptilolite and mordenite in G-1 and between 10 and 60 percent clinoptilolite in G-3.[15] The greatest concentration of zeolites is near the top of the zone in both holes, more than 140 m above the present-day water table. It has been inferred, on the basis of similarities between fracture mineralogy and diagenetic mineralogy of the bulk-rock, that the water table may have been as much as 120 m higher than it is today in the northern part of the candidate area.[16] Na, K, Ca, and Mg have been redistributed within zone II from east to west across Yucca Mountain.[13] The Clinoptilolite- and mordenite-rich tuffs have gained Ca and lost alkalies (K and Na) in significant amounts, attributable to their proximity to Ca-rich rock and ground water east of the candidate area.[13] Redistribution of Rb and Sr is also likely to occur during diagenetic alteration of the rock mass.[17,18] In contrast, the distribution of Zr is believed to be unaffected by secondary alteration[18,19,20] and may provide an important first-order reference for discriminating between primary compositional characteristics and element redistribution resulting from diagenesis and weathering.

Rubidium

Rb concentrations range between 59 ppm and 186 ppm in G-1 and between 113 and 198 ppm in G-3 (fig. 3A). A high degree of variability over intervals of less than about 100 m is common in G-1, particularly within diagenetic zone II, which includes the Bullfrog and Tram Members of the Crater Flat Tuff and the dacite lava (fig. 3A). Rb concentrations less than 130 ppm are commonly associated with the uppermost and lowermost few meters of the major stratigraphic units where lithologies grade into nonwelded and bedded tuffs (fig. 3A). Rb concentrations typically exceed 150 ppm within moderately to densely welded zones and in the interior of the dacite lava (fig. 3A).

Rock intervals having low Rb concentrations closely correlate with those having low K concentrations (fig. 3A, 3B). Abrupt decreases in both Rb and K concentrations commonly correlate with local increases in clinoptilolite and mordenite content within diagenetic zone II (fig. 2B).[15] Rb concentrations vary significantly less in G-3, where, in general, the abundance of zeolites and clays is significantly less than

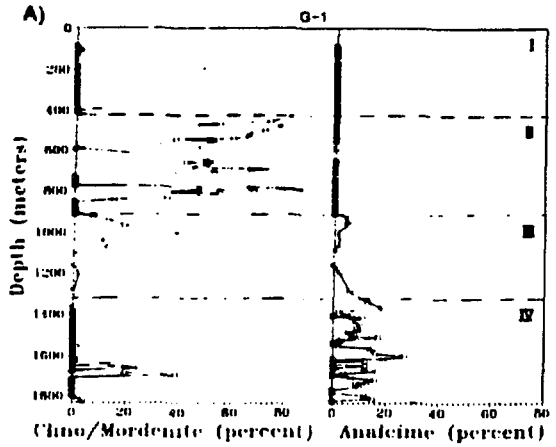

Figure 2. Distribution of (A) clinoptilolite/mordenite and analcime in G-1[15], (B) clinoptilolite and analcime in G-3[15], (C) smectite in G-1 and G-3[15]. Dashed lines denote approximate boundaries between zones of diagenetic alteration I, II, III, and IV[14].

in G-1. For example, Rb concentrations, averaging 159 ± 7 ppm (n=number of samples, n=15) are tightly clustered within the 130-m-thick moderately to densely welded zone of the Bullfrog Member of the Crater Flat Tuff in G-3, which is directly above the water table. The relative uniformity of Rb concentrations in the Bullfrog amd Topopah Spring Members suggests a strong resistance of thick moderately to densely welded zones that are above the present-day water table to trace-element redistribution resulting from devitrification and(or) secondary alteration.

Strontium

Sr content varies significantly with depth. Sr concentration increases from an average value of 31 and a range of 21 to 55 ppm (n=23) within the Topopah Spring Member to an average of 166 ppm (n=4) in the units a and b of the older tuffs (fig. 3C). In addition to this gradual increase with depth, intervals that show anomalously high Sr concentrations are present in (1) the lower part of the Tram Member and the dacite lava in G-1, (2) unit c of the older tuffs in G-1, and (3) the densely welded zone of the Bullfrog Member in G-3. The highest Sr concentration, 869 ppm, is near the middle of the dacite lava in G-1 (fig. 3C), which corresponds to a clay-rich interval in diagenetic zone III where smectite content is more than 60 percent (fig. 2C).[15] Unlike stratigraphic units directly above and below, the dacite lava is autobrecciated near its upper and lower contacts and contains an abundance of calcite-filled fractures.[5]

Alternatively, high concentrations of Sr may be an artifact of a change in rock type from the high-silica rhyolitic tuffs to lava of dacitic composition and trace-element contamination from abundant lithic inclusions. Although the highest Sr concentration is in the dacite lava, anomalously high concentrations are also present in the lower half of the overlying Tram Member. These high Sr values correlate with abundant lithic inclusions of intermediate composition in the lower half of the Tram Member, providing a potential source for elemental contamination of bulk-rock samples from this interval.[5] In G-1, within clay-rich unit c of the older tuffs, Sr increases abruptly from about 340 ppm to a maximum of 594 ppm over an interval of about 100 m (fig. 2C, 3C).

In G-3, Sr concentration generally increases with depth, except from 674 m to 685 m, where Sr concentrations are as high as 459 ppm within the upper part of the moderately to densely welded zone of the Bullfrog Member. Although the upper limit of the anomaly is poorly constrained, Sr values abruptly decline below a depth of 685 m, forming a tight cluster of values that averages 127 ppm and ranges between 102 and 157 ppm (n=12) within the thick densely welded zone of the Bullfrog Member (fig 3C). This anomaly is well above the present-day water table, does not appear associated with abrupt changes in welding or zeolite and smectite content, and, therefore, may be related to primary composition.

Zirconium

Except for a few anomalies, Zr concentrations also increase slightly with depth. In both coreholes, Zr concentrations average 102 ppm and range between 83 and 117 ppm (n=23) within the Topopah Spring Member and average 150 ppm (range of 98 to 168 ppm, n=8) within the Lithic Ridge Tuff (fig. 3D). As with Sr, Zr concentrations are high in the lower part of the Tram Member, in the dacite lava of G-1, in unit c of the older tuffs in G-1, and in the densely welded zone of the Bullfrog Member in G-3 (fig. 3D). Zr concentrations show only slightly less variability within the thick welded zones than in nonwelded to partially welded zones. Intervals that have relatively high Sr concentrations also have relatively high Zr concentrations. This correlation between high concentrations of Sr and relatively immobile Zr within localized intervals suggests either primary composition or a significant redistribution of Sr and Zr resulting from smectitic alteration of tuffs at Yucca Mountain.

Strontium Isotopes

As part of our study, we also prepared and analyzed composite samples of major stratigraphic units in G-1. Present-day $^{87}Sr/^{86}Sr$ values decrease with depth from 0.71603 in the Topopah Spring Member of the Paintbrush Tuff to 0.70892 in unit c of the older tuffs (table 1). This decrease persists even after Sr values are corrected for in-situ growth of radiogenic ^{87}Sr following deposition of the ash flows. Initial $^{87}Sr/^{86}Sr$

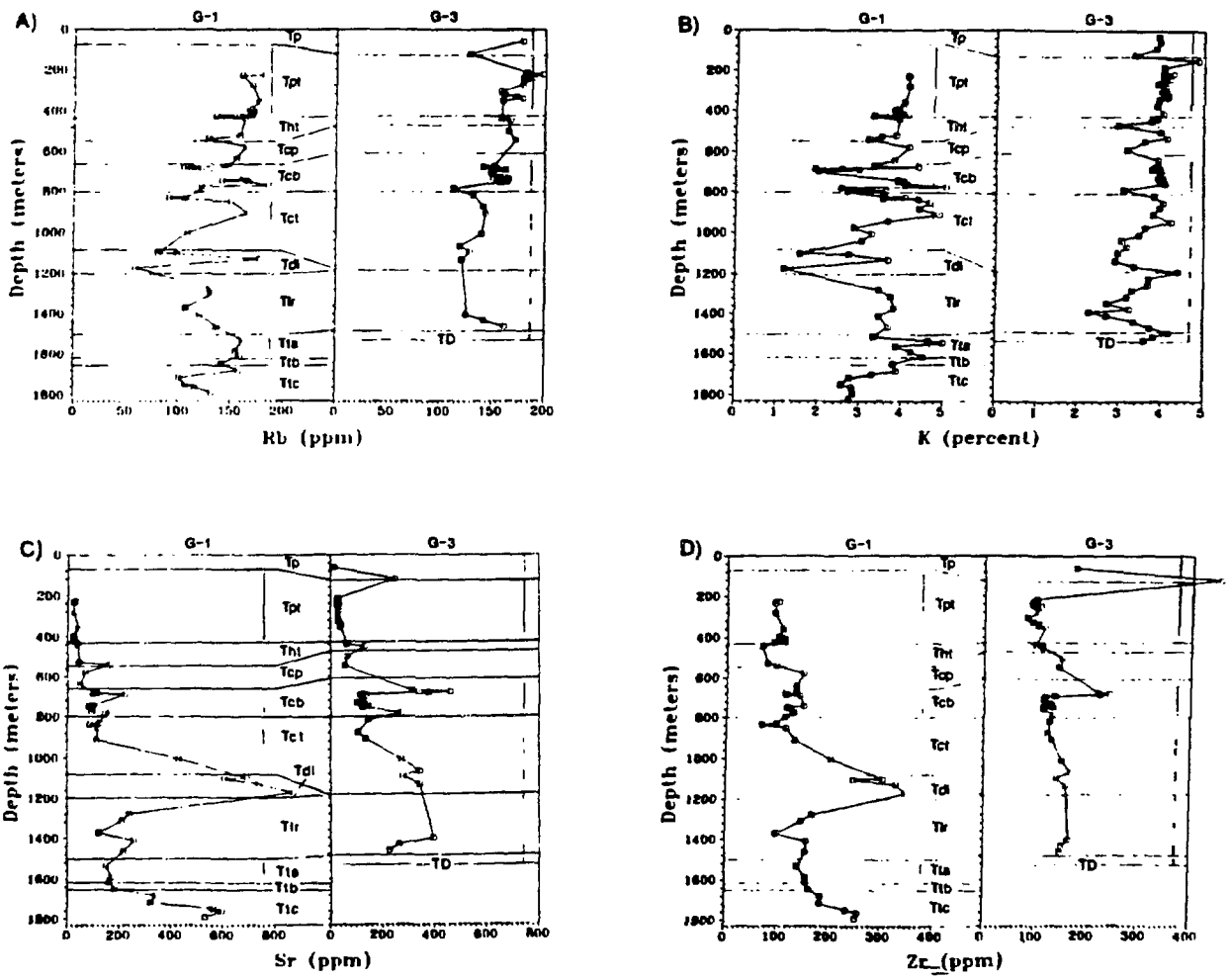

Figure 3. Distribution of (A) Rb, (B) K[7,8], (C) Sr, and (D) Zr in G-1 and G-3, Yucca Mountain. Upper Paintbrush Tuff, Tp; Topopah Spring Member of the Paintbrush Tuff, Tpt; rhyolite of Calico Hills, Tht; Prow Pass Member of the Crater Flat Tuff, Tcp; Bullfrog Member of the Crater Flat Tuff, Tcb; Tram Member of the Crater Flat Tuff, Tct; dacite lava of G-1, Tdl; Lithic Ridge Tuff, Tlr; older tuffs and lavas, Tta, Ttb, Ttc. Discontinuous vertical lines denote zones of moderate to dense welding[4,5]; TD indicates total depth of G-3.

TABLE 1.–Minor and trace elements and Sr-isotopic data of composite samples from G-1 (values in parentheses after each stratigraphic unit denote number of samples included in each composite sample; IR(Sr) denotes initial Sr isotopic ratio; ppm denotes parts per million; ages of stratigraphic units are based on $^{40}Ar/^{39}Ar$ geochronologic determinations[21] and stratigraphic interpolation)

Stratigraphic unit	Depth to top of unit (meters)	K (wt. percent)	Rb (ppm)	Sr (ppm)	Zr (ppm)	$^{87}Rb/^{86}Sr$	Age (Ma)	$^{87}Sr/^{86}Sr$	IR(Sr)
Topopah Spring Member(12)	72	3.57	178	25	110	20.81	12.8	0.71603	0.71225
rhyolite of Calico Hills(4)	435	3.50	164	70	84	6.81	12.9	0.71328	0.71203
Prow Pass Member (2)	549	3.95	162	54	149	8.62	13.0	0.71172	0.71013
Bullfrog Member (16)	662	3.42	151	136	138	3.22	13.1	0.70953	0.70893
Tram Member (11)	804	3.72	138	210	149	1.91	13.6	0.70974	0.70937
dacite lava (4)	1084	2.05	109	752	339	0.42	13.7	0.70928	0.70920
Lithic Ridge Tuff (6)	1203	3.42	132	248	169	1.54	13.9	0.70909	0.70879
older tuffs-unit a (6)	1506	4.39	159	168	149	2.74	14.0	0.70955	0.70901
older tuffs-unit b (1)	1622	3.72	138	196	159	2.04	14.0	0.70921	0.70880
older tuffs-unit c (7)	1656	3.10	133	527	340	0.73	14.0	0.70892	0.70878

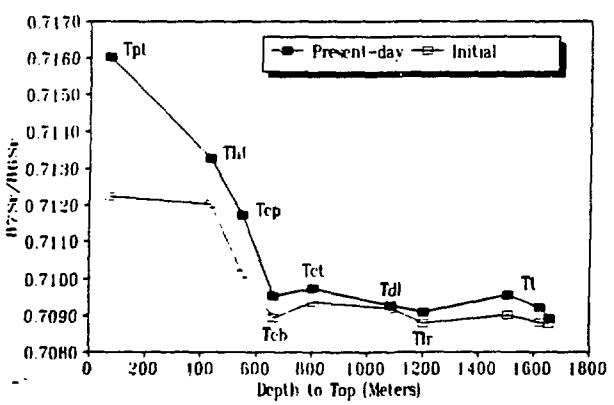

Figure 4. Present-day and initial $^{87}Sr/^{86}Sr$ ratios of composite samples from G-1, Yucca Mountain (upper Paintbrush Tuff, Tp; Topopah Spring Member of the Paintbrush Tuff, Tpt; rhyolite of Calico Hills, Tht; Prow Pass Member of the Crater Flat Tuff, Tcp; Bullfrog Member of the Crater Flat Tuff, Tcb; Tram Member of the Crater Flat Tuff, Tct; dacite lava of G-1, Tdl; Lithic Ridge Tuff, Tlr; older tuffs and lavas, Tt)

(IR(Sr)) values increase abruptly above the Bullfrog Member of the Crater Flat Tuff (fig. 4). Composite samples of units younger than the Bullfrog Member have IR(Sr) ratios between 0.7101 and 0.7122, whereas the Bullfrog Member and older units have lower IR(Sr) ratios between 0.7088 and 0.7094. The general increase in Sr concentration with depth, coupled with significantly lower present-day $^{87}Sr/^{86}Sr$ and IR(Sr) values, is consistent with a massive influx of Sr from water derived from the Paleozoic carbonate aquifer. Although not corresponding exactly to the time-integrated average for the interval, when superimposed on the Phanerozoic marine Sr isotope curve[22] for an age interval represented by the regional carbonate aquifer in southern Nevada[23], they clearly overlap with the marine values.

CONCLUSIONS

Preliminary assessment of the distribution of Rb, Sr, and Zr on a bulk-rock scale at Yucca Mountain reveals significant lateral and vertical anisotropy that can be provisionally correlated with variations in welding, primary compositions, diagenetic alteration, and eruptive contamination. The distributions of Rb and K appear to be significantly affected by diagenetic alteration. Conspicuous local high concentrations of Sr parallel those of Zr, which indicate primary compositional variations or the effects of smectitic alteration. Rb and K trends, as well as Sr-isotopic

compositions support open-system behavior due to diagenetic alteration, facilitated by reaction and interaction with ground water. We expect Sr in ground water of the regional carbonate aquifer to carry a marine Paleozoic signature. The IR(Sr) ratios from the Bullfrog Member of the Crater Flat Tuff and older units are within the range of Paleozoic marine values, suggesting that the source of much of the Sr and, by analogy, the Ca, was ground water from a regional carbonate aquifer. The higher IR(Sr) ratios from units overlying the Bullfrog Member suggest a significant change in the rock-water interaction and appear inconsistent with claims of a higher paleo-water table at Yucca Mountain. Verification of these interpretations will require detailed comparative studies of unaltered and altered sample pairs from stratigraphically equivalent tuff and lava units, as well as studies of the Paleozoic section, secondary minerals along fractures, and various ground water systems, to fully characterize past element redistribution at Yucca Mountain.

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